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14. ABSTRACT

The objectives of this research project have been to characterize the degradation of various types of polymers under simulated space (low-earth orbit (LEO)) conditions and to develop polymers for spacecraft coatings which have improved survivability in LEO. Many polymers have been tested including kapton, polyethylene, fluoromers, polyhedral oligomeric silsequioxane (POSS)-containing copolymers and others. The testing was performed in an ultrahigh vacuum system which contained an atomic oxygen (AO) source and a vacuum ultraviolet (VUV) source. In some studies the polymers were also exposed to energetic electrons and ions. The chemical alterations occurring during the degradation was monitored using X-ray photoelectron spectroscopy (XPS). All polymers exhibit large chemical changes. The POSS-containing polymers are particularly interesting for space applications because they form a thin silica layer which protects the underlying polymer from further degradation.

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Final Performance Report – AFOSR Grant No. F49620-01-1-0257
Professor Gar B. Hoflund

The objectives of this research were to improve the performance of a hyperthermal oxygen atom (AO) source, add an ultraviolet source to the AO chamber to simulate low-earth orbit (LEO), characterize polymers during erosion by AO and UV which are or may be important in space applications and development of new types of polymers with improved space survivability. These objectives have been met. The AO flux has been increased by a factor of 10 by redesigning the lens assembly and is now 10 times that encountered in LEO. An ultraviolet source has been added to the UHV system and studies have been carried out to investigate chemical alterations at polymer surfaces induced by VUV radiation. Many different polymers have been examined in these studies including polyimides, fluoromers and polyhedral oligomeric silsequioxane (POSS) copolymers. The POSS-containing polymers exhibit excellent resistance to AO erosion because a thin silica layer forms on the surface after C and H are removed. This layer protects the underlying polymer from further erosion.

Synthesis and Atomic Oxygen Erosion Testing of Space-Survivable POSS (Polyhedral Oligomeric Silsequioxane) Polyimides accepted by High Performance Polymers

This paper presents several characterization studies of the surfaces of newly synthesized POSS-containing polyimides before and after exposure to atomic oxygen (AO). AO exposure testing was conducted independently at the University of Florida and Montana State University revealing comparable data. The exposed surfaces were characterized using X-ray photoelectron spectroscopy, and atomic oxygen erosion rates were calculated using stylus surface profilometry. The data indicates that AO induced erosion of polyimides containing POSS is drastically reduced and is eventually halted as a result of a passivating silica layer formed on the surface of the polymer.

In-Situ Atomic Oxygen Erosion Study of Fluoropolymer Films using XPS: Journal of Applied Polymer Science 92(2004)1977

The surfaces of a homologous series of fluoropolymers were characterized in-situ using X-ray photoelectron spectroscopy before and after a 15-minute exposure to the flux produced by the AO. The linear polymers investigated in this study include high-density polyethylene (HDPE), poly (vinyl fluoride) (PVF), poly (vinylidene fluoride) (PVdF), and, poly (tetrafluoroethylene) (PTFE). They possess a similar base structure with increasing fluorine-to-carbon ratios of 0, 1:2, 1:1 and 2:1 respectively. No interaction of the AO with the non-fluorine containing linear polymer HDPE was detected over this short exposure. However, a correlation exists between the chemical composition of the fluorinated polymers and the induced chemical and structural alterations occurring in the near-surface region as a result of exposure to AO. The data indicate that AO exposure results in a substantial decrease in the near-surface fluorine concentration. The fluorine-

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to-carbon ratios of PVF, PVdF and PTFE decreases during the 15-minute AO exposure by 68, 39 and 18.5% respectively.

Chemical Alteration of Poly (tetrafluoroethylene) (Teflon) Induced by Exposure to Hyperthermal Atomic Oxygen: Journal of Physical Chemistry B 108(2004)00

In this study the erosion of poly (tetrafluoroethylene) (Teflon) by hyperthermal atomic oxygen (AO) has been examined using X-ray photoelectron spectroscopy (XPS). The initial F/C atom ratio of 1.66 decreases to 1.15 after a 2-hr exposure to a flux of 2×10^{15} atoms/cm²-s AO with an average kinetic energy of 5 eV. The F/C atom ratio is further reduced to a value of 0.90 after a 25-hr exposure. The high-resolution XPS C 1s data indicate that new chemical states of carbon form as the F is removed, and that the relative amounts of these states depends upon the F content of the near-surface region. The states are most likely due to C bonded only to one F atom and C bonded only to other C atoms. Exposures of the AO-damaged surface to O₂ results in chemisorption of a very small amount of O (~0.8 at%) indicating that large quantities of reactive sites are not formed during the chemical erosion by AO. Further exposure to AO removes this chemisorbed oxygen. After exposing the AO-exposed surface to air for 90 min, both O and H₂O are chemisorbed, and the F/C at ratio is reduced to 0.68. Another 46 hrs of AO exposure results in removal of these species and a further decrease in the F/C at ratio to 0.58.

Chemical Alteration of Poly (tetrafluoroethylene) (Teflon) Induced by Exposure to Ultraviolet Radiation accepted by Journal of Polymer Science

In this study the chemical alteration of poly (tetrafluoroethylene) (Teflon) by ultraviolet radiation (UV) (115-400 nm) has been examined using X-ray photoelectron spectroscopy (XPS). The initial F/C atom ratio of 1.98 decreases to 1.65 after a 2-hr exposure. The F/C atom ratio is further reduced to a steady-state value of 1.60 after a 74-hr exposure. The high-resolution XPS C 1s data indicate that new chemical states of carbon form as the F is removed, and that the relative amounts of these states depends upon the F content of the near-surface region. The states are most likely due to C bonded only to one F atom, C bonded only to other C atoms and C which have lost a pair of electrons through emission of F. Exposures of the UV-damaged surface to O₂ results in chemisorption of a very small amount of O indicating that large quantities of reactive sites are not formed during the chemical erosion by UV. Further exposure to UV removes this chemisorbed oxygen. Comparison of XPS data indicates that the mechanisms of chemical alteration by UV radiation and hyperthermal atomic oxygen (AO) are different as expected.

Erosion Study of Poly (Ethylene Tetrafluoroethylene) (Tefzel) by Hyperthermal Atomic Oxygen: Macromolecules 37(2004)6013

In this study the erosion of poly (ethylene tetrafluoroethylene) ETFE (Tefzel) by hyperthermal atomic oxygen (AO) has been examined using X-ray photoelectron spectroscopy (XPS). Initially the Tefzel film had F/C and O/C atom ratios of 0.74 and 0.04, which decrease to 0.17 and 0.01 respectively after a 2-hr exposure to a flux of 2×10^{15} atoms/cm²-s AO with an average kinetic energy of 5 eV. The F/C atom ratio is further reduced to 0.02 with longer AO exposures essentially producing a graphitic or amorphous carbon-like layer with a carbon content greater than 90 at%. Longer AO exposures do not alter the composition of this layer significantly. Exposure of the AO-damaged surface to O₂ or air nearly doubles the oxygen content in the near-surface region. This is due to dissociative oxygen adsorption at reactive sites formed at the polymer surface during AO exposure. Further exposure to AO removes this chemisorbed oxygen. C-H bonds are important sites for attack during erosion by hyperthermal AO.

Erosion Study of Poly (vinyl fluoride) (Tedlar) by Hyperthermal Atomic Oxygen: Applied Surface Science 239(2004)367

In this study the erosion of poly (vinyl fluoride) (Tedlar) by hyperthermal atomic oxygen (AO) has been examined using X-ray photoelectron spectroscopy (XPS). Initially the Tedlar film had F/C and O/C atom ratios of 0.45 and 0.11, which decrease to 0.018 and 0.04 respectively after a 2-hr exposure to a flux of 2×10^{15} atoms/cm²-s AO with an average kinetic energy of 5 eV. This exposure essentially produced a graphitic or amorphous carbon-like layer with a carbon content greater than 90 at%. Longer AO exposures do not alter the composition of this layer significantly. Exposure to O₂ or air nearly doubles the oxygen content in the near-surface region. This is due to dissociative oxygen adsorption at reactive sites formed at the polymer surface during AO exposure. Further exposure to AO removes this chemisorbed oxygen.

Chemical Alteration of Poly (Vinyl Fluoride) Tedlar® Induced by Exposure to Vacuum Ultraviolet Radiation: submitted to Applied Surface Science

In this study the chemical alteration of poly (vinyl fluoride) Tedlar® by vacuum ultraviolet radiation (VUV) (115-400 nm) has been examined using X-ray photoelectron spectroscopy (XPS). The initial F/C atom ratio of 0.34 decreases to 0.17 after a 2-hr exposure. The F/C atom ratio is further reduced to a steady-state value of approximately 0.04 after a 24-hr exposure. Similarly, the O/C atom ratio is reduced from 0.08 to 0.05 and then to 0.02 during these two exposures. As the F and O are removed by VUV exposure, the C concentration increases from 70.5 to 82.0 and then to 94.6 atom % thus forming a graphitic or amorphous carbon-like layer which erodes more slowly than the virgin Tedlar surface. Exposure of the VUV-damaged surface to O₂ results in chemisorption of O, indicating that reactive sites are formed during the chemical erosion by UV. Further exposure to VUV removes this chemisorbed oxygen but a subsequent

exposure to air at atmospheric conditions causes a threefold increase in O chemisorbed at the surface. Comparison of XPS data indicates that the mechanisms of chemical alteration by VUV radiation and hyperthermal (~5 eV) atomic oxygen (AO) are similar.

Chemical Alteration of Poly (tetrafluoroethylene) TFE Teflon® Induced by Exposure to Primary Electrons and 1 keV He⁺: submitted to **Chemistry of Materials**

In this study the chemical alteration of poly (tetrafluoroethylene) TFE Teflon® by primary electrons and 1.0 keV He⁺ ions has been examined by using X-ray photoelectron spectroscopy (XPS). The initial F/C atom ratio of 1.99 decreases to 1.41 after a 2-hr exposure to the electron flux. The F/C atom ratio is further reduced to a steady-state value of 1.48 after 48 hours of electron exposure. A 2-hr exposure to He⁺ decreases the initial F/C atom ratio from 2.07 to 1.79 it is further reduced to 1.12 after a 19-hr exposure. The high-resolution XPS C 1s data indicate that new chemical states of carbon form as the F is removed and that the relative amounts of these states depend upon the F content of the near-surface region. These states are most likely due to C bonded only to one F atom, C bonded only to other C atoms and C that have lost a pair of electrons through emission of F⁻. Exposures of the electron-damaged and He⁺-damaged surfaces to research-grade O₂ results in chemisorption of a very small amount of O indicating that large quantities of reactive sites are not formed during the chemical erosion by electrons. Further exposure to the electron or He⁺ flux quickly removes this chemisorbed oxygen. Exposure of the He⁺-damaged surface to air at room temperature results in the chemisorption of a larger amount of O than the O₂ exposure but no N is adsorbed. Comparison with the studies above indicates that AO results in the most damaged followed by UV, ions and electrons.